Automatic Measurement System of Hydrated Sodium Silicate Composition Analysis

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Abstract

Sodium silicate is one of the most successful inorganic binder. Along with the broad application of sodium silicate for domestic and industrial purposes, the composition analysis, include modulus (m), ratio of $SiO_2:Na_2O$, $Na_2O\%$, $SiO_2\%$, and solid-containing content, is important for the products strength and service life. However, it is perplexing to operate, inefficient and low precision for traditional standard testing method of these parameters. In this study, an automatic measurement system of sodium silicate composition analysis, with the potential electrode for potentiometer titration, micro-controller, PCB, heater, stirrer, printer and micro peristaltic pump, was developed according to the determine method principle. The end-points of pH value in the two titrating steps, first was 4.3 and second was 6.0, were set in the micro-controller to control the reaction in the processing of the sodium silicate composition analysis. And all the potential signals of the pH electrode were transited in the special PCB for the micro-controller.

Keywords: Hydrated sodium silicate, Composition analysis, Potentiometer titration

1. Introduction

Soluble silicates ($Na_2O \cdot mSiO_2$) are one of the oldest and most benign industrial chemicals [1]. There is now a demand for binders to be environmentally friendly and allow for better process efficiencies while still being reasonably priced [2]. In recognition of these increased performance requirements, sodium silicate based formulations have been broadened to offer increased performance.

Hydrated sodium silicate can be used in casing mold sands, welding rod, grouting material, steel corrosion prevention and others [3-4]. Sodium silicate mould sand can be classified as environmentally friendly process and it is widely used in steel casting [5]. And the hydrated sodium silicate its parameters will influence the derived products strength and life. The most important property of sodium silicate is the modulus (m), also

called weight ratio of $SiO_2:Na_2O$. Sodium silicate is commercially produced in the ratio range of 1.5 to 3.2. And the modulus is the most important one but it is the most difficult to determine. For example, in casting production, the use of higher modulus hydrated sodium silicate sands has the advantages of low residual strength, short CO_2 blowing time, and has good moisture absorption and surface stability. But the working time of higher modulus hydrated sodium silicate sands is shorter than the lower one. So the use of lower modulus hydrated sodium silicate sands is popular in the factory[6-7].

If the modulus can be determined, the other parameters, such as $Na_2O\%$, $SiO_2\%$, and solid-containing content can be easily conversed in certain formula. But the current methods of measuring the modulus of hydrated sodium silicate are manual titration, especially the titration end-point of indicator color is determined by naked eye, sometimes the repeating the titration

and test cycles is longer, so the naked eye will be tired to get the end-point. And the reactant of NaF has a low solubility in the cool water, so the SiO_2 content may be lower[8]. To solve those problems, the authors put forward a new method of automatic measurement system for the modulus of hydrated sodium silicate based on potentiometer titration technology.

2. The basic principle of hydrated sodium silicate composition analysis

Many traditional measuring methods were described in the in the literatures using six steps to determine the modulus, which referred to GB/T4209-2008 [8]. There are three reactions in this determination process:
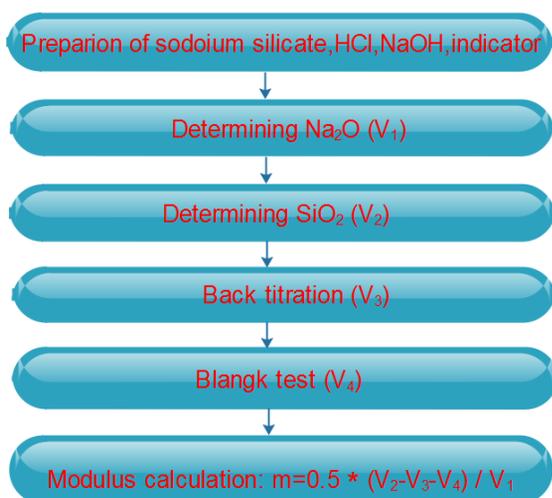
$$Na_2O \cdot mSiO_2 + 2HCl + (m-2)H_2O \rightarrow 2NaCl + mH_2SiO_3 \qquad (1)$$

$$H_2SiO_3 + 6NaF + H_2O \rightarrow Na_2SiF_6\downarrow + 4\ NaOH \qquad (2)$$

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad (3)$$

Fig.1 Traditional measuring method steps

The six steps are showed as Fig 1: (1). Preparing of the solution of methyl red indicator, sodium silicate, HCl standard solution (0.5mol/L), NaOH standard solution (0.5mol/L). (2.) Determining Na_2O by the indicators to show the reaction of HCl (V_1) and Na_2O according to the No.1 reaction. (3). Determining SiO_2 (V_2). A certain amount of NaF is added to produce NaOH as No.2 equation shows after Na_2O determination. So the amount SiO_2 can be conversed by the consumption of HCl (V_2) according to the No.3 reaction. (4). Back titration (V_3). The excessive HCl (V_3) was added for accurate determination according to the GB/T4209-2008, so a few imposed NaOH was used to neutralize HCl in the back titration. (5). Blank test (V_4). The blank test should be done to eliminate the influence of alkaline NaF on the HCl consumption (V_4). (6). Modulus calculation. The modulus can be calculated as the following only when the four standard solution data (V_1, V_2, V_3, V_4) are ready:

$$m = n(SiO_2)/n(Na_2O) = 0.5 \times (V_2 - V_3 - V_4)/V_1$$

From many duplicate tests, it can be seen that these methods have some disadvantages. First, the testing steps were complex, which needed indicator and four standard solution consumption data. Secondly, it is difficult to determine the end point of the titration of silicon dioxide by observing the color change of the indicator, in fact it was hard to catch the color-changing ranges of the indicators in the several parallel tests because experimenters' eyes would be tired to color for long-term observation. But all the end points of titration were important especially for V_2. Thirdly, the use of NaF would not arise experimenter recognition because its solubility in cool water was so low that it would cause the under-reaction of NaF and H_2SiO_3. Lastly, back titration was time-consuming and unnecessary.

3. The automatic measurement system of hydrated sodium silicate composition analysis
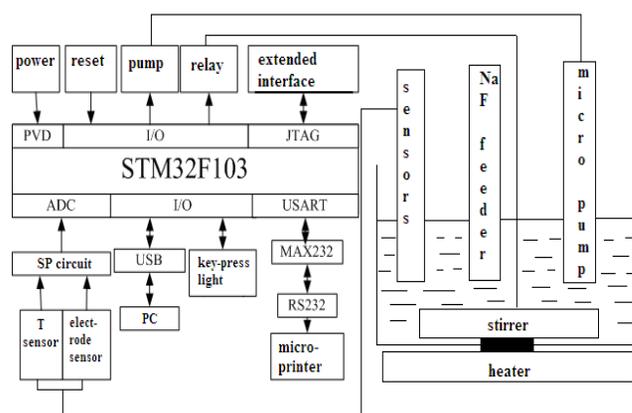

Fig.2 The automatic measurement system

An automatic measurement system of hydrated sodium silicate composition analysis was developed according to the above principle by employing the potentiometer titration to judge the end point [9]. This system, showed as Fig.2, was composed of the metal pH potential electrode to avoid fluorine ion corrosion (ASI-PG100 antimony electrode, made in Shanghai Lei Magnetic Company), micro-controller (STM32F103), PCB, printer, micro peristaltic pump (The model number is BQ50-1J,0.0002-20ml/min, made in Jinan Ailaibao Company), heater and stirrer. It can be seen that the back titration (V_3) was canceled for employing the high precision potential electrode and micro-controller [10].

The potential signal, which obtained by high precision pH antimony electrode instead of human naked eye, was used to collect the pH data, and micro peristaltic pump was used to replace manually adding and titration. In the end, the micro-controller would complete data processing and control the end point. The two important of end point pH value was 4.3 for No.1 equation and 6.0 for No.3 equation from our many experiments.

The two data were stored in the micro-controller and compared to the data from antimony electrode real-time.

4. The new determining steps of automatic measurement system

The determining steps included solution preparation and automatic measurement:
1. Preparation of hydrated sodium silicate and HCl standard solution. About 10ml liquid sodium silicate (about 5g for solid sodium silicate) and water was added to 500ml volumetric flask to prepare testing solution, and about 50ml of this solution was extracted into the above reactor with stirrer and heater. The HCl standard solution with the concentrate of 0.5mol/L was prepared as the standard method.
2. Automatic determining by this device. The power of the automatic measurement system was turned on when hydrated sodium silicate testing solution, HCl standard solution and NaF powder were added in the certain designed container. And the testing results will be printed in 20 minutes.

The flowing was the specific process in the automatic measurement system:(1). The HCl standard solution was pumped into the reactor by the micro peristaltic pump, and the reaction of HCl and Na_2O was fast for the stirrer, so the micro-controller can stop the micro peristaltic pump when the pH value of reaction solution reaches 4.3 after micro-controller judged the titration end-point of pH value, which was set in the micro-controller in advance. And the V_1 result will be recorded in the micro-controller and printed in the micro printer. (2). Automatic adding 5g solid NaF and heating the reaction solution. The NaF was added by the NaF feeder to the reaction solution with the pH value of 4.3, and then the mixture reaction to produce NaOH by the stirrer and heater for sufficient reaction, where the feeder, stirrer and heater also controlled by the micro-controller. (3). Again, the HCl standard solution was pumped into the reactor, and the micro-controller can stop the micro peristaltic pump when the pH value of reaction solution reached 6.0, so the V_2 result will be recorded and printed. (4). Automatic determining of V_3 in the blank test. About 5g solid NaF and $(50+ V_1 +V_2)$ ml water was added in the empty reactor and then heating and stirred, the HCl standard solution was pumped into the reactor as above, and the micro-controller can stop pumping when the pH value reached 6.0, so the V_3 result will be recorded and printed. (5). Computing and printing results. When the pumping stopped, the micro-controller would computer the modulus (m), $Na_2O\%$, $SiO_2\%$, and solid-containing content, in which m= $0.5\times$ (V_2-V_3) $/V_1$.

5. Results discussions and conclusions

Two testing sodium silicate sample was determined in this system, and the results were showed as Tab.1 comparing to traditional method. The two tested hydrated sodium silicate sample of new method were common in the factory, and there was few high modulus hydrated sodium silicate used in the factory. In traditional method, the same hydrated sodium silicate of middle modulus was used according to the new method. Average (ā) and rang (R) were used to evaluate the results fluctuation value, and the lower R, the more accurate of the testing.

It is noted that the modulus (2.051) of the traditional method was lower than the new one (2.131) for the NaF and H_2SiO_3 under-reaction in cool water. And many aspects, such as high temperature and stirring for saturated NaF solution, were taken into considering for sufficient reaction in the new method. So the new method of automatic measurement system had the advantages of high precision and time saving, where the time consuming of new method (20min) was one-sixth of the tradition method(120min).

The indicator and back titration were canceled in the new automatic measurement system, and the key technologies of new method were using blank test end-point as the end point of titration and employing electric potential signal of the pH electrode to replace the indicator as the judgment of titration end-point. This system will be widely used in the casting and sodium silicate factory because it only needs preparing hydrated sodium silicate and HCl standard solution.

Table 1.
The testing results between the new method and traditional method

Method	$V_1/$ mL	$V_2/$ mL	$V_3/$ mL	m	Average ā & R
New method (20min)	11.38	35.89	0.80	1.542	$\bar{a}^1$=1.543, R^1=0.003
	11.40	35.99	0.81	1.542	
	11.37	35.94	0.80	1.545	
New method (20min)	9.18	39.92	0.80	2.131	$\bar{a}^2$=2.131, R^2=0.001
	9.20	40.05	0.82	2.132	
	9.15	39.80	0.80	2.131	
Traditional method (120min)	9.2	36.5	0.8	1.940	$\bar{a}^3$=2.051, R^3=0.214
	9.1	38.4	0.9	2.060	
	9.1	40.2	1.0	2.154	

Acknowledgement

Referenes

[1] Rabbii, A. (2001). Sodium silicate glass as an inorganic binder in foundry industry. *Iranian Polymer Journal*. 10(4), 229-235.

[2] Stachowicz, M., Pałyga, Ł.& Kępowicz, D. (2020). Influence of automatic core shooting parameters in hot-box technology on the strength of sodium silicate olivine moulding sands. *Archives of Foundry Engineering*. 20(1), 67-72.

[3] Huafang, W., Wenbang, G. & Jijun, L. (2014). Improve the humidity resistance of sodium silicate sands by estermicrowave composite hardening. *Metalurgija*. 53(4), 455-458.

[4] Nowak, D. (2017). The impact of microwave penetration depth on the process of heating the moulding sand with sodium silicate. *Archives of Foundry Engineering*. 17(4), 115-118.

[5] M. Stachowicz, K. Granat, & D. Nowak. (2011). Application of microwaves for innovative hardening of environment-friendly water-glass moulding sands used in manufacture of cast-steel castings. *Archives of Civil and Mechanical Engineering*. XI(1), 209-219.

[6] Zhu, CX. (2007). Recent advances in waterglass sand technologies. *China Foundry*. 4(1), 13-17.

[7] Masuda Yuki, Tsubota Keiji, Ishii Kenichi, Imakoma Hironobu, Ohmura Naoto. (2009) Drying rate and surface temperature in solidification of glass particle layer with inorganic binder by microwave drying. Kagaku Kogaku Ronbunshu. 35(2). 229-231.

[8] Standardization Administration of the P.R.C. (2008). GB/T4209-2008, Sodium silicate for industry use[S]. Beijing, China Standard Press.

[9] Bourikas K., Kordulis C. & Lycourghiotis A. (2005). Differential potentiometric titration: Development of a methodology for determining the point of zero charge of metal (Hydr) oxides by one titration curve. *Environmental Science & Technology*. 39(11), 4100-4108.

[10] Fan ZT, Liu M, Wang HF, Long W, Hu XT. (2010). Chinese Patent No. 201010558029.3. Beijing, China National Intellectual Property Administration.